

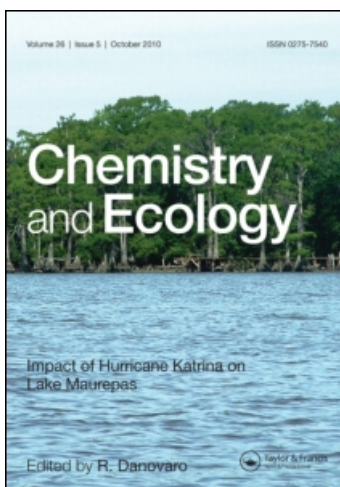
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## Chemistry and Ecology

Publication details, including instructions for authors and subscription information:

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### Heavy metal distribution and speciation in the Northern Adriatic Sea

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Online publication date: 14 September 2010

**To cite this Article** Zago, Cristina , Capodaglio, Gabriele , Barbante, Carlo , Giani, Michele , Moret, Ivo , Scarponi, Giuseppe and Cescon, Paolo(2010) 'Heavy metal distribution and speciation in the Northern Adriatic Sea', *Chemistry and Ecology*, 18: 1, 39 – 51

**To link to this Article:** DOI: 10.1080/02757540212689

**URL:** <http://dx.doi.org/10.1080/02757540212689>

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## HEAVY METAL DISTRIBUTION AND SPECIATION IN THE NORTHERN ADRIATIC SEA

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(Received 1 November 2000; In final form 23 March 2001)

In the present study the concentrations of cobalt, copper, iron, manganese, zinc were analysed and the speciation of copper and zinc performed, with a summer and winter sampling, for two areas in the Northern Adriatic Sea and crossing at the farthest zones of the Po river-sea water interface. Results show that when salinity increases the concentrations of all investigated metals (with the exception of cobalt) present some degree of biogeochemical cycling. Copper is the element whose dissolved phase has the highest importance in metal transport across the salinity gradient. Results of speciation analysis demonstrate that the presence of excess amounts (5–8 fold) of unbound ligands confers a buffering capacity for potential inputs of dissolved metals into the Northern Adriatic Sea. The speciation of both copper and zinc in the dissolved phase was dominated by organic complexation.

*Keywords:* Heavy metals; distribution; Adriatic Sea

### 1. INTRODUCTION

Massive biological and chemical recycling of nutrient and metal constituents occurs in most estuaries (Burton and Liss, 1976; Paulson *et al.*, 1993), and chemical removal of trace metals from water to sediments occurs frequently when fresh and saline waters are mixed (Paulson *et al.*, 1993; Millward and Glegg, 1997; L'Her Roux *et al.*, 1998). Nutrients are also removed from the water by phytoplankton growth and, in relatively unpolluted estuaries, the physical mixing seems to be the dominant process affecting nitrate concentrations (Burton and Liss, 1976). Although the coupling of nutrient and trace metals cycling has been widely confirmed in oceans (Bruland, 1980; Bruland, 1989), in estuaries, observations of trace metal removal by biological processes are few

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(Church, 1986). In many estuaries, the presence of strong physical mixing and local inputs, which also differ among estuaries (Abe and Matsunaga, 1988; Paulson *et al.*, 1993; Owens and Balls, 1997), does not allow us to observe and generalise the coupling of nutrients and metals. Moreover, in some estuaries the biological processes dominate the trace metal cycling (Paulson *et al.*, 1993), in others riverine and anthropogenic inputs dominate the internal cycling (Millward and Glegg, 1997; Owens and Balls, 1997).

Biological processes can strongly influence the chemistries of trace metals, and, in turn metals can influence plankton production and community structure (Bruland *et al.*, 1991). The interactive influences are particularly important for metals of the first transition series, which are required by phytoplankton for various metabolic functions (Mn, Fe, Co, Cu and Zn). A deficiency of these "bioactive" trace metals may limit plankton production (Brand *et al.*, 1983) and an excess of certain of these same metals may inhibit plankton growth (Brand *et al.*, 1986). It is known that "bioactive" trace metal concentrations can be quantified only by determining the particular form of metals in waters, normally the free ion concentration, and so enabling the study of their speciation (Bruland *et al.*, 1991).

In estuarine environments, the chemical form in which metals are present during physical mixing is assumed to play an important role in their geochemical cycle (L'Her Roux *et al.*, 1998). Factors which have been demonstrated to play a major controlling role in the trace metal behaviour include complexation with dissolved organic (van den Berg *et al.*, 1987) and inorganic (Comans and van Dijk, 1988) species, and interactions with particulate material (Turner *et al.*, 1993; Owens and Balls, 1997) and sediments (Evans *et al.*, 1977). It has been shown that the partitioning of metals between the dissolved and particulate phase, due to adsorption, desorption, precipitation and flocculation, takes place frequently within the estuarine zone (Sholkovitz, 1976; Hoyle *et al.*, 1984; Li *et al.*, 1984; Stumm, 1987; L'Her Roux *et al.*, 1998), and that the rate and extent to which this occurs depend on many factors including metal reactivity and the estuarine hydrodynamics (Morris, 1990; Millward and Turner, 1995). For all these reasons, the metal speciation in waters has become an important step in determining metal behaviour in the estuarine environment.

In the present study the concentrations of cobalt, copper, iron, manganese, zinc and the speciation of copper and zinc have been performed, with a summer and winter sampling, in two areas localised in the Northern Adriatic Sea and crossing the further zones of the Po river-sea water interface (Fig. 1). Copper and zinc were selected for speciation analysis because these two bioactive metals provide the best examples of the importance of trace metal-biota interactions (Bruland *et al.*, 1991). This paper focuses on the speciation of metals and on their partitioning between dissolved and particulate phases during the mixing of fresh and salty waters with the aim of studying their cycling and their interactions with the biological pool.

## 2. MATERIALS AND METHODS

Samples were collected during the periods 16 June–2 July, 1996 and 11 February–1 March, 1997. During June, 1996 (Fig. 1), a total of 14 water samples were collected at different depths at 6 stations (AB1, CD13, EF24, GH30, MN40, OP43). During

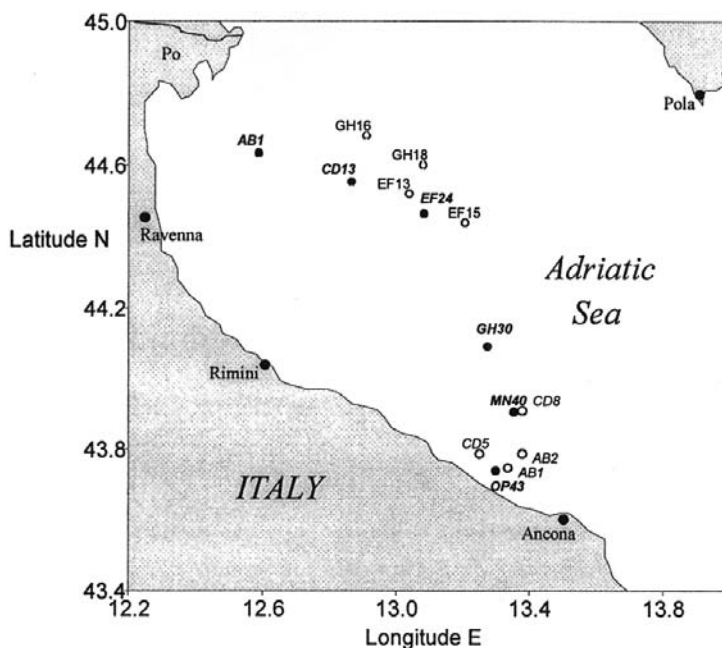


FIGURE 1 Map of the sampling stations of the June–July, 1996 (●) and February–March, 1997 Cruises (○).

February, 1997, 17 water samples were collected at 8 stations (EF13, EF15, GH16, GH18, AB1, AB2, CD5, CD8). In stations AB1, AB2, CD8 the samplings were repeated after two days.

In the collection of surface water the operator moved away from the ship with a rubber dinghy and gathered samples using a submersible Teflon pump for temporary storage in a cleaned high capacity polyethylene container (20–50 l). Deep water samples (more than 10 m from the surface) were collected using a sampling bottle immersed to the desired depth by a Kevlar hydrowire. Go-Flo bottles of 30 l capacity internally coated with Teflon were used. Filtration of samples through a polycarbonate membrane filter of 0.4  $\mu\text{m}$  pore size (Nucleopore) was carried out immediately after sampling inside the clean laboratory on board. For the filtration of surface and deep water samples a Teflon apparatus developed for on-line pressure filtration (Sartorius SM16540, Gottingen, Germany) was used. Samples were stored frozen ( $-20^{\circ}\text{C}$ ) at natural pH.

Copper and zinc determinations were performed by Differential Pulse Anodic Stripping Voltammetry (DPASV) in a Class-100 laboratory. A detailed description of the electrochemical cell and of the instrumentation assembly used was reported by Scarponi *et al.*, 1996, where the methodology to detect copper concentration is reported.

The measurements of total dissolved metal concentration were carried out on acid-digested,  $\text{pH} \approx 2$ , samples for at least 48 hours. For sample acidification, 100  $\mu\text{l}$  hydrochloric acid of 32% Ultrapure, NIST (National Institute of Standards and Technology, USA) were added to 50 ml of sample (Nürnberg *et al.*, 1976). The multiple

standard addition method was used for quantification. The total zinc concentration was carried out using a deposition potential of  $-1.30$  V against Ag/AgCl/KCl sat. The sample was buffered at  $\text{pH} \sim 4.5$  by sodium acetate solution (4 ml of 2 M solution in about 20 ml of sample) to avoid hydrogen discharge. Moreover, gallium (100  $\mu\text{l}$  of gallium chloride solution, 0.06 M) was added to about 20 ml of sample at the beginning of analysis, to avoid Zn-Cu intermetallic compound formation.

The speciation methodology involves the titration of organic ligands present in the sample by additions of the metal to be studied. By reworking of the titration data it is possible to determine the ligand concentration and the relative conditional stability constant (Ruzic, 1982; van den Berg, 1984; Scarponi *et al.* 1996). The titration to study the complexation of each metal is carried out individually on separate aliquots of the sample, freshly defrozen and untreated.

Samples collected during June, 1996 were analysed for dissolved copper, cobalt, iron, manganese and zinc concentrations, at the Analytical Chemistry Department at Turin University. The determination of iron and manganese was performed by ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrometry). Analysis of copper, cobalt and zinc were performed by AAS (Atomic Absorption Spectrometry, Perkin Elmer Z5100 with electrothermic atomiser HGA600), coupled with a Flow Injection System (FIAS-200, Perkin Elmer). The system involves a preconcentration step and a saline matrix separation by metal complexation with ammonium pyrrolidin dithiocarbamate (APDC) followed by adsorption of the complex by a C18 column (Porta *et al.*, 1991). Samples collected during February, 1997 were analysed for dissolved concentration of copper, cobalt, iron, and manganese by ICP-MS (Inductively Coupled Plasma Atomic Emission Spectrometry) after sample dilution (1:5), to reduce saline matrix interference, and acidification with 1:100 nitric acid NIST (32%) (Barbante *et al.*, 1998). In order to test analysis results, copper values were compared with those obtained by duplicate samples performed by DPASV.

Due to sampling problems encountered in June, 1996, the analysis of particulate material was unfortunately not possible.

Filters collected during February, 1997 were analysed for particulate ions (Al, Co, Cu, Mn, Fe and Zn) in the laboratory of the ICRAM Institute, Chioggia. The filters were totally digested with  $\text{HNO}_3/\text{HCl}/\text{HF}$  in teflon bombs using a microwave digester (Milestone 1200) and determined by a Spectro Modula ICP-AES.

Temperature, salinity and fluorescence determinations were performed in the northern area by the ISDGM-CNR, Venice, and in the southern area by the Istituto Universitario Navale, Naples.

### 3. RESULTS AND DISCUSSION

#### 3.1. Oceanographic Data

During the June–July, 1996 campaign, waters in the northern coastal area samples reflected the vertical stratification typical of a warmer and less saline surface waters. Salinity and temperature data showed that during that summer sampling, the Po river stratified at the surface for about 30 nautical miles from the river delta. The thermocline and pycnocline were almost coincident for coastal stations with a sharp gradient at

about 10 m depth. The highest fluorescence values (which can be considered a biomass index) have been observed at this depth, indicating that in the mixing zone, the biological activity is high. Stations further than 30 nautical miles from the Po river delta present a superficial pycnocline (less than 10 m depth) and a deeper thermocline (more than 20 m depth). During the same period, in the southern area, coastal waters with characteristic similar to those originating from the River Po are confined within 5 nautical miles from coast. In this area only superficial station OP43 could be considered to be influenced by Po river waters.

The temperature and salinity measurements of February 1997, performed in the northern area, showed that the less saline and colder waters of the River Po reached 30 nautical miles from the river delta in winter too. The thermocline and pycnocline of coastal samples are again present at 10 m depth. Higher fluorescence values were present in superficial and coastal waters but the highest values corresponded to water masses with less saline and intermediate temperature waters at about 30 nautical miles from the river delta, where fresh water encountered sea waters. This zone also proved to be the highest turbidity zone.

### 3.2. Total Dissolved and Particulate Metals

Total dissolved and particulate metal concentrations obtained from samples collected during the two campaigns are reported in Table I. Obtained metals concentrations are in the range observed in Northern Adriatic, during summer 1994, by Tankere and Statham (1996).

In the northern area, total dissolved metal distributions in both sampling campaigns (Fig. 2) showed a concentration related to the salinity of the waters, and, with the exception of iron, the lower values were obtained in the higher salinity waters. Therefore, higher metal concentrations were obtained in near-shore superficial waters, with concentration decreasing from in-shore to off-shore and from surface to deep waters. Iron concentrations in samples, collected in June, 1996, were below the detection limit of the ICP-AES technique ( $5 \text{ nmol l}^{-1}$ ). The concentrations of iron during the winter campaign decreased, similarly to the other metals, from superficial to deeper samples, but they were higher in off-shore stations than coastal ones (Fig. 2b). Other authors (Camusso *et al.*, 1997) analyzing waters in the delta of the River Po found higher iron concentrations ( $12\text{--}87 \text{ nmol l}^{-1}$ ) in a riverine sample than coastal ones ( $5\text{--}33 \text{ nmol l}^{-1}$ ), and they suggested a removal of this metal by precipitation as iron (III) processes. Looking at iron concentrations measured in the northern area (ranging from 1 to  $9 \text{ nmol l}^{-1}$ ) surely the largest amount of riverine iron has been removed from the dissolved phase within the first miles from the coast. Anyway, in the observed salinity range, iron increased toward the sea end-member.

In summer, 1996, dissolved manganese showed increased concentrations in bottom waters of the coastal samples (Fig. 2a) and in winter it had relatively high concentrations in the mixing regions. Iron also showed a maximum in the highest mixing region. This result is probably due to iron and manganese release from riverine particulate material (enriched in heavy metals) due to the increased salinity gradient and/or to different chemical characteristics related with the origins of the marine water masses. Unfortunately very little is known on the small scale (Northern Adriatic)

TABLE I Concentrations of total dissolved and particulate metals in the all sampling stations. dissolved iron detection limit ( $5 \text{ nmol l}^{-1}$ ). Particulate detection limits ( $\text{nmol l}^{-1}$ ): Mn = 0.1; Co = 0.1; Cu = 0.2; Zn = 0.2; Zn = 0.9; Al = 3; Fe = 7

Station	Depth (m)	Dissolved metals						Particulate metals					
		Cu	Zn	Fe	Mn	Co	Cu	Zn	Fe $\times 10^3$	Mn	Co	Al $\times 10^3$	
		(nmol/l)						(nmol/l)					
June–July 1996													
AB1	0.5	7.0	13.2	<d.l.	16.5	0.74	–	–	–	–	–	–	
AB1	12	7.5	34.5	<d.l.	18.8	0.56	–	–	–	–	–	–	
AB1	22	4.7	26.2	<d.l.	55.9	0.50	–	–	–	–	–	–	
CD13	7	3.1	3.1	<d.l.	6.7	0.65	–	–	–	–	–	–	
CD13	25	2.6	8.6	<d.l.	6.1	0.12	–	–	–	–	–	–	
EF24	10	2.6	7.8	<d.l.	2.5	0.27	–	–	–	–	–	–	
EF24	25	5.1	7.2	<d.l.	6.1	0.07	–	–	–	–	–	–	
GH30	0.5	2.9	16.9	<d.l.	4.6	0.08	–	–	–	–	–	–	
GH30	15	3.9	6.6	<d.l.	5.8	0.27	–	–	–	–	–	–	
GH30	35	5.2	10.8	<d.l.	10.8	0.40	–	–	–	–	–	–	
MN40	0.5	7.4	16.2	<d.l.	39.7	0.50	–	–	–	–	–	–	
MN40	25	4.4	5.5	<d.l.	2.1	0.10	–	–	–	–	–	–	
OP43	0.5	10.4	14.9	<d.l.	46.1	0.11	–	–	–	–	–	–	
OP43	7	9.1	3.5	<d.l.	53.0	0.40	–	–	–	–	–	–	
February–March 1997													
GH16a	1	10.4	6.4	3.5	49	0.92	7.7	23	1.03	18	0.6	3.7	
GH16a	15	5.3	5.9	1.4	8.8	0.58	<d.l.	2	0.02	<d.l.	<d.l.	0.09	
EF13a	1	5.8	4.0	6.0	60	1.64	0.2	4	0.23	3	0.1	0.89	
EF13a	20	5.3	3.9	1.6	9.6	0.52	<d.l.	<d.l.	0.04	18	<d.l.	0.14	
GH18b	10	3.3	4.9	1.5	8.0	0.58	<d.l.	<d.l.	0.3	17	<d.l.	1.14	
GH18b	20	4.2	3.9	5.9	28	0.37	<d.l.	<d.l.	0.02	18	<d.l.	0.07	
EF15b	1	4	4.1	8.8	14	0.37	<d.l.	<d.l.	0.02	<d.l.	<d.l.	0.09	
EF15b	25	2	3.8	2.8	9.3	0.49	<d.l.	<d.l.	0.01	18	<d.l.	0.03	
AB1c	1	10.1	3.7	2.0	21	1.25	0.7	5	0.59	10	0.2	2.13	
AB2a	1	8.2	5.4	6.9	21	0.60	6.7	13	0.79	14	0.4	2.99	
AB2b	5	8.3	4.9	7.0	17	1.00	1.1	9	0.49	10	0.3	1.96	
AB2a	10	5	4.5	9.2	21	0.27	5.6	3	0.79	14	0.4	3.04	
AB2b	10	5.5	3.5	1.8	14	0.49	0.9	6	0.74	11	0.5	2.87	
CD5a	1	11.1	5.3	6.7	38	1.29	2.4	13	1.11	16	0.7	4.23	
CD5b	1	10.6	3.4	9.4	27	0.89	0.7	6	0.42	8	0.3	1.53	
CD8a	1	5.2	5.3	3.2	16	0.64	0.7	3	0.4	7	0.3	1.56	
CD8b	1	4	3.4	–	–	0.49	0.2	2	0.27	7	0.2	1.01	

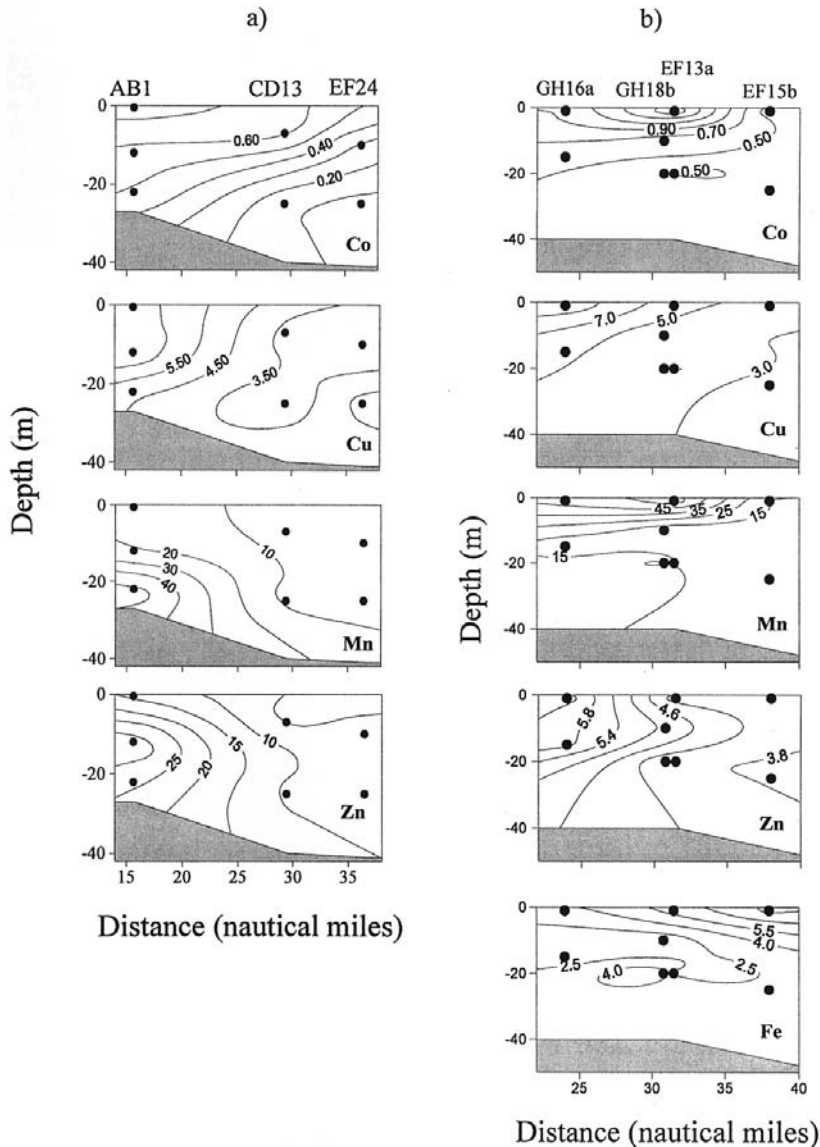


FIGURE 2 Total dissolved metal concentrations (nM) in the northern area obtained from (a) the June–July, 1996 and (b) the March–February, 1997 campaign.

hydrodynamics of these regions. In the summer sampling, zinc increased at intermediate depth, and its maxima were coincident with those of fluorescence.

In the southern area, as at the northern stations, higher dissolved cobalt, copper and manganese concentrations were found in both samplings in the low salinity region within 5 nautical miles from the coast (the cobalt trend for the June, 1996 sampling is not completely clear). Zinc showed a marked vertical concentration profile, with higher concentrations in superficial waters. Iron concentrations increased where the salinity gradient is sharper, as also found by Kenney-Kennicutt and Presley (1986).



The analysis of particulate material performed in the northern area in the February, 1997 sampling (Fig. 3) showed that metals enter in the Adriatic Sea basin linked to riverine particulate material and that there is a significant spatial variation of the metal content in the mixing region. With the exception of manganese, samples less affected by Po water influence had metal values below the detection limit (Co and Cu concentrations were below the detection limit in all samples with the exception of the GH16 and EF13 surface samples). Metal particulate concentrations were compared to aluminium content to evaluate the crustal contribution in the particulate composition. Therefore, comparisons between the metal and aluminium distributions give indications on the origin of the particulate metals. The concentration of aluminium decreased going off-shore. Because this element behaves conservatively and is not affected by changes in physico-chemical conditions occurring in the estuary, it may be assumed that the aluminium decrease is due to a progressive dilution of suspended matter of continental origin with particles of marine origin (Regnier and Wollast, 1993). Results in the northern area clearly show that while iron and partially zinc trends are almost

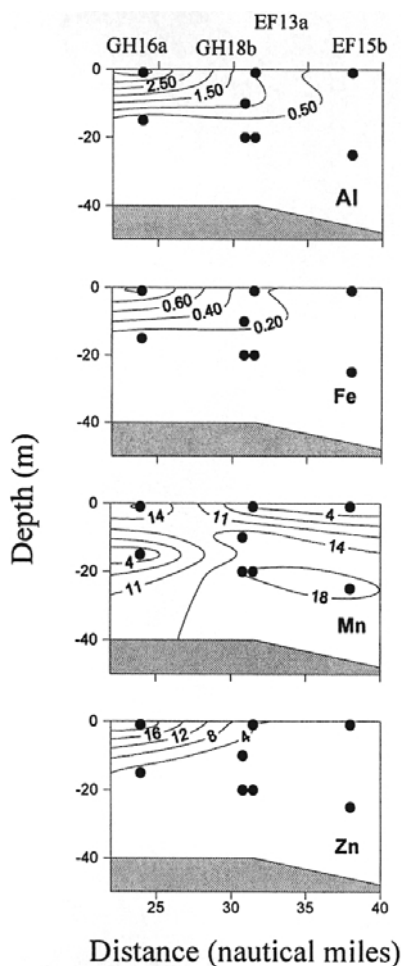


FIGURE 3 Particulate metal concentrations (nM) in the northern area obtained from the March–February, 1997 campaign.

coincident with those of aluminium (although limited data are available), particulate manganese is highly enriched in deeper sea waters.

Particulate metal trends in the southern area showed higher concentrations in riverine waters for all the observed metals. The cobalt and iron trends were almost coincident with that of aluminium, indicating that the particulate transport across this area of the estuary is not highly affected by geochemical changes but is mostly due to the dilution of particulate material. Copper, manganese and zinc showed a geochemical behaviour different to that of aluminium. To compare the relative importance of dissolved and particulate metal transport to the sea, the partitioning of copper, cobalt, iron, manganese and zinc between these phases was determined by the partition coefficient,  $K_d$ . Unfortunately, analysis of the  $K_d$  for metals of the northern grid was not possible because a large part of the sea metal concentrations were below the detection limit. The relative importance of the dissolved phase in metal transport was ranked  $\text{Cu} > \text{Co} > \text{Mn} > \text{Zn} \gg \text{Fe}$ , similarly to Keeney-Kennicut and Presley (1986). The metal partition coefficients,  $K_d$  (dissolved metal concentration/particulate metal concentration), obtained for copper and zinc, indicates a higher relevance of the dissolved phase than the particulate one toward the off-shore stations (for copper high dissolved concentrations are also present in the near shore region). Cobalt and manganese particulate phases are important in deeper waters, while for iron is a in-shore waters.

Although metals decrease with increasing salinity, plotting total dissolved metals against salinity, metals generally showed a non-conservative behaviour in both sampling, with the exception of cobalt, which shows an almost linear decrease with salinity. These results clearly show that when riverine water mixes with sea water the concentrations of all investigated metals (with the exception of cobalt) present some degree of biogeochemical cycling.

### 3.3. Copper and Zinc Speciations

Distributions of the ligand concentrations of copper and zinc in the two areas and in the different campaigns are shown in Figure 4. No labile metal concentrations [ $\text{Cu}^{+2}$ ] or [ $\text{Zn}^{+2}$ ] were generally detected in the observed samples, and the total dissolved metal concentration was exclusively present as organically complexed metals. It is likely that ligands determined in the observed area, due to algal exudates, extracellular ligands or organic chelators, may decreased the free metal concentrations, as also observed in other estuaries (Kozelka *et al.*, 1997).

Many authors reported that copper in ocean waters is complexed by two classes of ligands, the first of which is stronger and related to marine phytoplankton, particularly to the presence of cyanobacteria (Brand *et al.*, 1986; Moffett *et al.*, 1990). The second class of ligands has, in oceans, a more homogenous distribution and it is probably related with refractory organic matter (Coale and Bruland, 1988; Coale and Bruland, 1990). In this study the first class of ligands was not detectable. Two hypotheses are possible: 1) the ligand concentration was lower than the detection limit; 2) the initial copper concentration was high enough to saturate the ligand, and therefore the titration procedure revealed only one class of ligand (even if the first ligand is present in the sample). Further titration curve elaboration will be necessary to obtain a definitive quantification of the first class of ligand. For these reasons, results showed in Figure 4

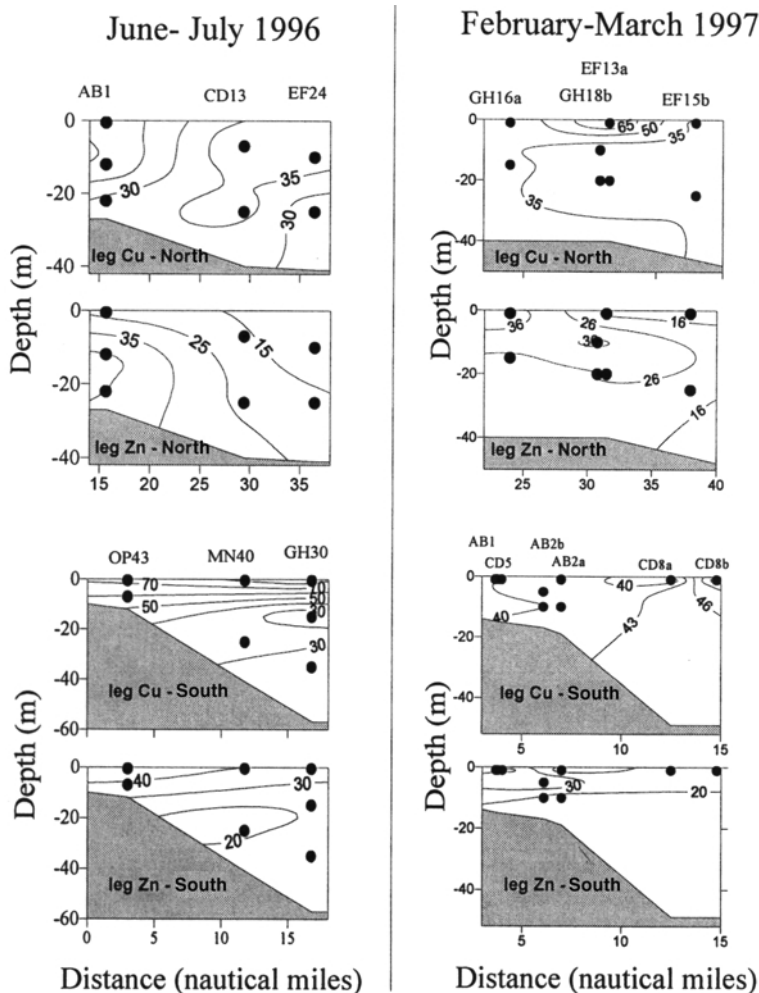


FIGURE 4 Ligand concentrations (nM) in both areas and in the two campaigns.

represent the total copper ligand concentration present in the sample without distinguishing between the two classes.

The copper ligand trends in the two samplings in the northern area (Fig. 4) present maxima at about 30 nautical miles from of River Po, where mixing between riverine and sea waters occurred (highest salinity gradient). During the summer and winter sampling the copper ligand concentrations proved generally higher in sea waters than coastal waters, with the exception of the winter sampling in the northern area, where a ligand concentration maximum was observed at 30 miles from Po river delta. This result leads us to hypothesise that the copper ligand has a marine origin.

In contrast to the copper ligand, the zinc ligand concentrations resulted in both samplings, with generally higher concentrations in coastal waters at intermediate depths. Moreover, a similar distribution between zinc ligand and fluorescence was observed. Presumably, the zinc ligand also has a phytoplankton origin, but not ne-

cessarily all the phytoplankton species contribute to its presence. The different nature of the two metal ligands is also shown by the different conditional stability constant obtained by the elaboration of the titration curve.

The metal ligand concentrations were much higher (5–8 fold) than those of the dissolved metal concentrations, as also found in other coastal environments (Kozelka *et al.*, 1997). This is important when considering that ligands can regulate the free metal ion activity acting as a buffer for dissolved metals present in the water column of this estuarine environment.

### 3.4. Conclusions

Taking into account all the examined data it is possible to summarise the following metal geochemical behaviours. Iron arrives in this area of the estuary linked to particulate material and it seems displaced from the solid towards the dissolved phase where the salinity gradient is high. Manganese has a similar geochemistry, but this metal, conversely to iron, proved to be enriched in the particulate phase of deeper sea waters. While dissolved zinc in summer was enriched at an intermediate depth, in winter it reached maximum concentration in surface waters and concentration decrease with depth was less evident than for other metals. The zinc peak at intermediate depth is coincident with the highest fluorescence values, particularly during summer. The control of zinc cycling in biological processes has been observed in the oceans and has been correlated with silicate cycling (Bruland, 1980). In estuaries, zinc removal seems only to be observed when nutrients are removed to a significant degree of biological processes (Church, 1986; Hunter and Tyler, 1987). Cobalt featured a conservative behaviour and its concentrations in the water column seem to be affected only by dilution. By comparison with the other metals, copper was the element whose dissolved phase had the highest importance in metal transport across the salinity gradients.

Results of speciation analysis demonstrates that the presence of excess amounts of unbound ligands confers a buffering capacity for potential inputs of dissolved metals into the northern Adriatic Sea. The speciation of both copper and zinc in the dissolved phase was dominated by organic complexation. Only the zinc ligand concentration seemed directly related to biological activities. Further data elaborations are necessary for copper. Bruland (1989) speculated that organic complexation may help to keep zinc in solution, rather than allow it to be adsorbed into particles and so settling to sediments. This could be in accordance with our results where the amount of copper and zinc in the water column feature a non-conservative behaviour inside the estuary, showing a capacity of being recycled and maintained in the water column. The same author speculated (Bruland *et al.*, 1991) that some phytoplankton species may be able to assimilate organically complexed zinc to the exclusion of other phytoplankton species. The occurrence of this hypothesis in the northern Adriatic could be verified by comparing metal ligand trends with those of different phytoplankton species. Thus, the biological roles of bioactive metals in this coastal estuarine region need to be better studied because the combination of macronutrients and trace metals may be simultaneously controlling biological production. This feedback between biological and chemical systems, widely observed in oceans, may be of importance in controlling and maintaining productivity and influencing species composition in high-nutrient areas.

### Acknowledgements

The authors would like to thank Dr. A. Bergamasco, of the ISDGM, CNR, Venice, and Prof. G. Spezie, Istituto Universitario Navale, Naples, which provided the oceanographic data. Thanks also to Prof. E. Mentasti and Dr. O. Abollino of the laboratory of the Analytical Chemistry Department of Turin University, for having performed the ICP-AES and AAS metal analysis in dissolved samples of June, 1996 sampling. Financial support was provided to Dr. Cristina Zago by the MAS3 CT95 0021 Project of the European Union. This work was supported by the Italian Ministry of University and Scientific and Technological Research (MURST) and the National Research Council (CNR) in the framework of the PRISMA II – Biogeochemical Cycles Research Project.

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